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(11) Publication number: **0 450 897 A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91302855.1**

(51) Int. Cl.⁵: **B22F 3/10**

(22) Date of filing: **02.04.91**

(30) Priority: **03.04.90 JP 88955/90**
03.04.90 JP 88956/90
12.04.90 JP 96867/90
20.02.91 JP 47534/91

(43) Date of publication of application:
09.10.91 Bulletin 91/41

(84) Designated Contracting States:
BE DE ES FR GB IT SE

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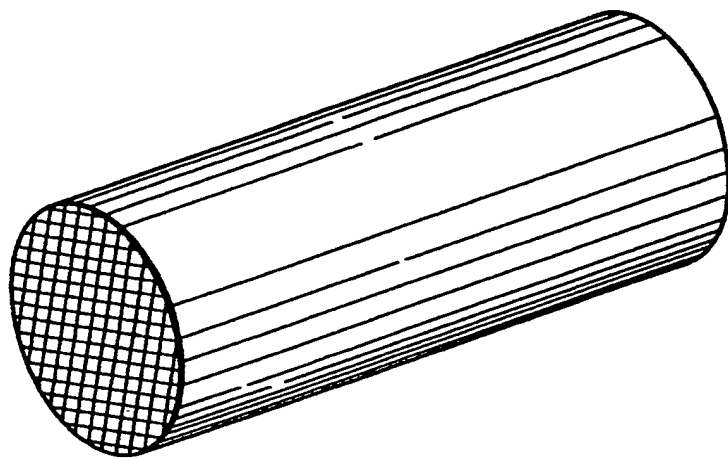
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(54) Heat-resistant metal monolith and manufacturing method therefor.

(57) A heat-resistance metallic monolith, which is manufactured by forming metal powders into a shape of a honeycomb structure and by sintering the shape, has a heat-resistant metal oxide coated on the surface of the cell walls and that of the pores thereof. Such a heat-resistant metallic monolith is manufactured by mixing metal powders, an organic binder and water to prepare a mixture, by forming the mixture into a shape of a desired honeycomb configuration, by sintering the shape in a non-oxidizing atmosphere at a temperature between 1000 and 1450°C and then by coating a heat-resistant metal oxide on a surface of the cell walls and that of the pores of the obtained sintered body.

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FIG.1



BACKGROUND OF THE INVENTION

Field of the Invention:

5 The present invention relates to a heat-resistant metallic monolith suitable for use as a catalyst carrier, a heater or a catalytic converter and a method for manufacturing such a heat-resistant metallic monolith.

Description of the Related Art:

10 Conventionally, porous ceramic honeycomb structures have been employed as catalysts or carriers for catalysts for removing, for example, nitrogen oxides, carbon monoxide and hydrocarbon present in the exhaust gas of internal combustion engines, such as automobiles, or filters for removing fine particles.

Whereas porous ceramic honeycomb structures continue to be a popular and useful material in such environments, there has been a desire to develop materials exhibiting greater mechanical strength and thermal resistance in hostile environments. Accordingly, a honeycomb structure produced by winding a metal plate in a corrugated fashion has been proposed in U.K. Patent 1492929 and used.

However, in this foil type metal honeycomb structure, the catalyst layers cannot be closely adhered to the metal substrate with a coating formed thereon because of its low porosity, and a ceramic catalyst readily peels off the metal substrate due to a difference in the thermal expansion between the ceramic catalyst and the metal substrate. Furthermore, telescope phenomenon readily occurs during the run cycle in which a metal to metal joint breaks and the metal substrate deforms in such a manner that it protrudes in the direction of the flow of gas. This may disturb safe running of the vehicle. Furthermore, in the manufacture of the foil type metal honeycombs, yield of the rolling process is low, inviting high production cost.

Honeycomb structures manufactured by forming metal powders and by sintering the formed body are also known. Such honeycomb structures have been proposed in, for example, United States Patent No. 4,758,272, Japanese Patent Laid-Open Nos. 57803/1982 and 57904/1982, Japanese Patent Publication No.6974/1982, and Japanese Utility Model Publication No. 67609/1988.

The honeycomb structure disclosed in United States Patent No. 4,758,272 has a composition essentially consisting, as analyzed in weight percent, of 5 to 50% Al, 30 to 90% Fe, 0 to 10% Sn, 0 to 10% Cu, 0 to 10% Cr and not more than 1% Mg and/or Ca. This honeycomb structure has a porosity of about 25 to 75% by volume and a predetermined cell density.

However, since this honeycomb structure has no heat-resistant metal oxide coating formed thereon and is therefore not heat-resistant, an oxide film may be partially formed on the honeycomb structure when it is used as a filter, differentiating the characteristics, such as thermal expansion or ductility, and increasing the possibility of the honeycomb structure being broken.

The honeycomb structure disclosed in Japanese Patent Publication No. 6974/1982 is manufactured by binding a large number of small honeycomb components made of powders of catalytic activating substances which act as catalysts for use in automobile exhaust emission control, such as nickel, copper and chromium. However, oxidation process is performed at a low temperature to achieve catalytic activity, and it is therefore impossible to accomplish sufficient heat-resistance. Furthermore, this honeycomb structure is not a monolithic body and may be broken due to vibrations given to it during the operation.

The metal honeycomb structures disclosed in Japanese Patent Laid-Open Nos. 57803/1982 and 57804/1982 are manufactured by preparing a mixture of metal powders, a thermosetting binder, a colloidal silica and so on, by forming the mixture into a honeycomb configuration by the extrusion and then sintering the shaped body after it has been hardened. Like United States Patent No. 4,758,272, however, Japanese Patent Laid-Open Nos. 57803/1982 and 57804/1982 do not disclose the provision of a heat-resistant coating. So, these metal honeycomb structures may be broken when used as, for example, a catalyst carrier.

In the preheater proposed in Japanese Utility Model Laid-Open No. 67609/1988, coated alumina readily peels off metal support due to a difference in thermal expansion between alumina and the metal support. Furthermore, a metal to metal joint of the metal substrate breaks during the operation, generating an electrically insulating portion and, hence, non-uniform flow of current and non-uniform heating.

Meanwhile, as for the heat-resistant film, it is described in U.S. Patent No. 4915751 to effect heat treatment twice at 900-960°C and 960-1,000°C to form alumina whiskers. This approach, however, has no effect for oxidation resistance. Also, in Japanese Patent Laid-Open No. 75040/1989, it is described to coat the surface layer of a base material (stainless steel) with an alkoxide or the like to form a protective film. However, the alkoxide is expensive; the base material is produced by melting and rolling and has no pores, and accordingly is not a porous alloy.

SUMMARY OF THE INVENTION

5 An object of the present invention is to provide a metallic honeycomb monolith which exhibits high resistance to heat, corrosion and oxidation and excellent ductility and a method of manufacturing such a metallic honeycomb monolith.

To this end, the present invention provides a heat-resistant metallic monolith comprising a metal monolith and a heat-resistant metal oxide coated on a surface of cell walls and that of pores in the metal monolith. The metal monolith is manufactured by forming metal powders into a shape of a honeycomb configuration and by sintering the shape.

10 The present invention also provides a method of manufacturing such a heat-resistant metallic monolith which comprises the steps of preparing a mixture of metal powders, an organic binder and water, forming the mixture into a shape of a desired honeycomb configuration, sintering the shape in a non-oxidizing atmosphere at a temperature between 1000 and 1450°C and coating a heat-resistant metal oxide on a surface of cell walls and that of pores of the obtained sintered body.

15 Extrusion, press shaping or slip casting etc. may be employed as forming or shaping method, and the extrusion (extruding method) is preferably employed.

The thus-obtained heat-resistant metallic monolith can be used as a catalyst carrier or a filter for removing the fine particles contained in the exhaust gas of automobiles. The heat-resistant metallic monolith of the present invention can also be employed to manufacture a heater. Manufacture of the heater is achieved by the provision of electrodes on the metallic monolith.

20 The present invention also provides a honeycomb heater comprising a metallic honeycomb structure produced by forming metal powders into a honeycomb configuration and by sintering said honeycomb; and at least two electrodes through which a current is supplied to said honeycomb structure to heat gas flow in passages formed in said honeycomb structure.

25 The heat-resistant metallic monolith of the present invention can also be employed to manufacture a catalytic converter. The catalytic converter may be manufactured by placing a catalyst on the metallic monolith and by providing electrodes on the metallic monolith. Also, the heat-resistant metallic monolith of the present invention can be employed to manufacture a catalytic converter which comprises a main monolith catalyst and a heater disposed adjacent to and upstream of the main monolith catalyst. This heater may be obtained by providing electrodes on the metallic monolith according to the present invention and by placing a catalyst on the metallic monolith, if necessary.

30 The present invention further provides a catalytic converter comprising a main monolith catalyst and a honeycomb heater disposed adjacent to and upstream of said main monolith catalyst, said honeycomb heater including a metallic honeycomb structure produced by forming metal powders into a honeycomb configuration and by sintering said honeycomb, and at least two electrodes provided on said metallic honeycomb structure.

35 In the preferred form, the metal monolith has a composition consisting essentially of 2.5 to 30% by weight of Al, 0 to 40% by weight of Cr and a balance of Fe.

In the process of the present invention, it is preferable to mix metal powders so that the resulting metal powder material comprises at least 30% by weight of a pure iron powder, because the material gives a sintered metal of improved corrosion resistance.

40 Further, by keeping the sintered material in a hydrogen-containing gas atmosphere of 500-1,300°C, there can be formed a dense alumina-based protective film of excellent adhesion and heat resistance.

BRIEF DESCRIPTION OF THE DRAWING

45 Fig. 1 is a perspective view of a honeycomb monolith according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

50 The heat-resistant metallic monolith according to the present invention has a heat-resistant metal oxide coated on a surface of cell walls and that of pores of a metal monolith.

Hence, the heat-resistant metallic monolith contemplated in the present invention exhibits high resistance to heat and oxidation and therefore minimizes the possibility of breakage which would occur when it is used as a catalyst carrier, filter, honeycomb heater or a catalytic converter for use in automobile exhaust emission control.

55 The composition of the metal monolith preferred in the present invention consists essentially, as analyzed in weight percent, of 2.5 to 30% Al, 0 to 40% Cr and a balance of Fe. The preferred proportion of Al is between 12 and 25% when the level of Cr is between 0 to 10%, and between 3 and 20% when the level of Cr exceeds

10%. The preferred level of Cr is between 10 and 25%. When the proportion of Al is less than 2.5%, resistance to oxidation at high temperature deteriorates. Inclusion of more than 30% Al increases brittleness of the products and deteriorates the characteristics thereof inherent in metals. Inclusion of more than 40% Cr further increases brittleness of the products and production cost.

5 In the metal monolith preferred in the present invention, 0 to 10% Sn and 0 to 10% Cu may also be present. Although presence of these elements lowers the sintering temperature, it deteriorates resistance to oxidation. The preferred proportion should therefore be at most 10% in total.

Preferably, the sum of Fe, Al and Cr constitutes 90% or more of the total composition. Below 90% of the sum of Fe, Al and Cr the heat-resistance and ductility of the metal monolith deteriorate.

10 Presence of Mg and Ca promotes the sintering. However, it deteriorates the characteristics of the metal monolith, such as resistance to oxidation, and it is therefore desirable for them not to be present.

The preferred contents of C and N in the metal monolith according to the present invention is respectively 1% or below, and that of O is 3% or below.

15 Any heat-resistant metal oxide can be coated on the surface of the cell walls and that of the pores in the metal monolith according to the invention. Examples of such metal oxides include Al_2O_3 and Cr_2O_3 .

The heat-resistant metallic monolith, having the above-described composition and structure, can be used as a catalyst carrier or a filter for removing the fine particles contained in the exhaust gas of automobiles.

20 The heat-resistant metallic monolith of the present invention can also be employed to manufacture a heater for domestic use, such as a hot air heater, or an industrial heater, such as a heater or a preheater for use in automobile exhaust emission control. Manufacture of these heaters or a preheater is achieved by the provision of electrodes on the heat-resistant metallic monolith.

25 The heat-resistant metallic monolith of the present invention can also be employed to manufacture a catalytic converter which is achieved by placing a catalyst on the metallic monolith and by providing electrodes on the metallic monolith. Also, the heat-resistant metallic monolith of the present invention can be employed to manufacture a catalytic converter which comprises a main monolith catalyst and a heater disposed adjacent to and upstream of the main monolith catalyst. The heater can be obtained by providing electrodes on the metallic monolith according to the present invention and by placing a catalyst on the metallic monolith, if necessary. These catalytic converters can be desirably employed in the control of an automobile exhaust emission.

30 The method of manufacturing the heat-resistant metallic monolith preferred in the present invention will be described below.

35 First, Fe powder, Al powder and Cr powder, or powders of alloys of these metals, with optional additions of Sn powder and Cu powder, are mixed to prepare a metal powder mixture having a composition essentially consisting of, as analyzed in weight percent, 2.5 to 30% Al, 0 to 40% Cr and a balance of Fe with the sum Al, Cr and Fe constituting 90% or more of the total composition. These metal powders may be produced by, for example, the carbonyl process, pulverization, atomization, reduction, or electrolytic method. The size of the metal powders is dependent on the wall thickness of the cells of the honeycomb structure. For example, in case of extrusion, it is practically desirable that the largest particle size be about two thirds of that of an extruding die slit. Preferably, the contents of C, O and N in the metal powder mixture are respectively 10% or less, 3% or less and 1% or less.

40 It is preferable to prepare, by mixing, the metal powder material so that the material comprises at least about 30% by weight of a pure iron powder, because the material gives a sintered material of improved corrosion resistance. The reason is presumed to be that debinding is made well resulting in lower carbon content. As the pure iron powder, there is preferable used an iron carbonyl powder produced by the carbonyl method, because it gives further improved debinding.

45 In case of the extrusion, subsequently, the metal powder mixture is blended into an organic binder, such as methyl cellulose or polyvinylalcohol, and water to produce a formable mixture, and that mixture is then formed into a shape of a desired honeycomb configuration by the extrusion.

50 When the metal powder mixture is blended into the organic binder and water, prior to the addition of water, an antioxidant, such as oleic acid, may be added to the metal powder mixture. Alternatively, powders of metals which are subjected to anti-oxidation process may be employed.

The use of oxide as a forming aid or the like disturbs sintering and is therefore undesirable.

55 Next, the shaped honeycomb body is sintered in a non-oxidizing atmosphere at a temperature ranging between 1000 and 1450°C. During the sintering in the non-oxidizing atmosphere containing hydrogen, the organic binder is decomposed and thereby removed with F or the like acting as a catalyst, and a good sintered body (a metal monolith) can therefore be obtained.

If the sintering temperature is lower than 1000°C, the sintering is achieved. Sintering conducted at a temperature higher than 1450°C causes deformation of the resulting sintered body or increases production cost and is therefore undesirable.

When a sinterable metal powder honeycomb monolith structure is to be sintered, the sinterable body is preferably encased in a sintering jig and thereby disposed close to or in contact with the jig. The sintering jig can be made of any material. Examples of such materials include metals, such as stainless steel, Mo and W, and ceramics, such as alumina, graphite and SiC.

The sintering time is appropriately determined such that the contents of C, N and O are within the above-described range. The preferred length of time is 2 hours or longer.

Thereafter, a heat-resistant metal oxide is preferably coated on the surface of the cell walls and that of the pores of the obtained sintered body by any of the following methods wherein:

(1) the metal monolith (sintered material) is kept in a hydrogen-containing gas atmosphere of 500-1,300°C.

(2) the metal monolith is subjected to the heat-treatment in an oxidizing atmosphere at a temperature ranging between 700 to 1200°C.

(3) Al or the like is plated on the surface of the cell walls and that of the pores of the sintered body (the metal monolith) (e.g., vapor plating) and that sintered body is subjected to the heat-treatment in an oxidizing atmosphere at a temperature between 700 and 1200°C.

(4) the metal monolith is dipped into a molten metal, such as Al, and that metal monolith is subjected to the heat-treatment in an oxidizing atmosphere at a temperature between 700 and 1200°C.

(5) alumina sol or the like is coated on the surface of the cell walls and that of the pores of the sintered body (the metal monolith) and that sintered body is subjected to the heat-treatment in an oxidizing atmosphere at a temperature between 700 and 1200°C.

To enhance resistance to heat and oxidation, heat-treatment conducted at a temperature ranging between 900 and 1200°C is preferred.

Of the above methods, the method (1) can form a dense alumina-based protective film of excellent adhesion and heat resistance and accordingly can give a metal monolith of excellent oxidation resistance and corrosion resistance.

In the method (1), the hydrogen-containing gas atmosphere preferably has a dew point of -70°C to -40°C.

Although the thus-obtained heat-resistant metallic monolith may have any honeycomb configuration, in a metallic monolith which is designed for use as a catalyst carrier, heater and catalytic converter, the cell density ranges from 6 to 1500 cells/in² (0.9 to 233 cells/cm²) with a cell wall thickness ranging from 50 to 2000 μ m.

To achieve sufficient mechanical strength and resistance to oxidation and corrosion, the porosity of the heat-resistant metallic monolith will be held between 0 and 50% by volume, and more preferably, less than 25% by volume. In a heat-resistant metallic monolith designed for use as a catalyst carrier, the porosity will be held 5% or above to ensure close contact between the metallic monolith and a catalyst layer.

Illustrating the heat-resistance of the heat-resistant metallic monolith with a heat-resistant metal oxide coated on the surface of the cell walls and that of the pores thereof according to the present invention, it is desired that an increase in the weight of a metallic monolith after being fired for 1000 hours in an atmosphere at 900°C be within 10% by weight of the total weight.

The term, "honeycomb monolith or honeycomb structure" is employed in this application to refer to an integral body having a large number of passages partitioned by the walls, as shown in Fig. 1. The passages have any cross-sectional form (cell shape), e.g., a circular, polygonal or corrugated form.

The present invention will further be illustrated in the following examples which are intended to be illustrative, but not limiting, of this invention.

Example 1

Fe powder prepared by the carbonyl process, Al powder prepared by atomization, Cr powder prepared by the electrolytic method, Fe-Al alloy powder prepared by pulverization and Fe-Cr alloy powder prepared by atomization, all having a particle size of 300 mesh or less, were mixed to prepare mixtures having the compositions listed in Table 1. Thereafter, each mixture was blended first into 5% by weight of methyl cellulose which served as an organic binder and 2% by weight of oleic acid which served as a lubricant and as an antioxidant of the metal powders then 20% by weight of water, to produce a formable admixture.

The obtained admixture was deaerated by means of a pug mill and then extruded through a die to form square cell honeycomb structure having a diameter of 100 mm, a cell wall thickness of 75 μ m and a cell density of 62 cells/cm².

After the shaped honeycomb structure was dried, it was sintered for 4 hours in hydrogen or hydrogen/argon atmosphere at a temperature between 1200 and 1450°C and then fired in an atmosphere for 2 hours at a temperature between 900 and 1100°C to form an oxide film on the surface thereof.

The porosity, oxidation resistance (represented by an increase in weight caused by firing in an atmosphere for 1000 hours at 900°C) and corrosion resistance (represented by a reduction in weight caused by dipping in

an aqueous solution of HCl having pH of 1 for 1 hour) of the obtained honeycomb structures were measured. The results of the measurements are also shown in Table 1. The porosity was measured by the Archimedes' method.

As can be seen from Table 1, inclusion of less than 2.5% by weight of Al is disadvantageous to provide heat-resistant alumina film and therefore deteriorates oxidation resistance. Inclusion of more than 30% by weight of Al , provides undersintering and deteriorates oxidation resistance.

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Table 1 (part I)

Example No.	Reference	Present invention								Reference	Present invention			Reference
		2	3	4	5	6	7	8	9		10	11	12	
Fe	98	95	88	78	70	83	70	55	78		75	68	55	35
Al	2	5	12	24	30	5	5	5	2		5	12	20	35
Cr	0	0	0	0	0	12	25	40	20		20	20	25	30
Batch Fe Powder	98	95	75	52	50	83	45	50	78		50	48	35	35
Al Powder	2	5			10	5	5		2			12		35
Cr Powder						12		40	20				25	30
(300 mesh or less)														
Fe-50Al Powder			24	48	40			10			10		40	
Fe-30Cr Powder							50				40	40		
Sintering temperature (°C) (Hydrogen atmosphere)	1200	1200	1200	1200	1200	1300	1300	1350	1250		1250	1300	1300	1300
Heat-treatment temperature (°C)	1000	1000	1000	1000	1000	900	900	900	1100		1100	1100	1100	1100
Porosity (%)	63	50	44	36	21	24	19	16	27		24	36	46	53
Resistance to oxidation (wt%) (An increase in weight caused by thermally aging 1000 hours at 900°C)	13.6	9.8	8.8	5.3	3.5	3.6	2.4	3.0	11.5		3.2	4.5	6.1	10.8
Resistance to corrosion (%) (Reduction of weight caused by dipping 1 hour in HCl solution of pH 2)	5.7	4.1	-	1.5	0.8	-	0.2	-	-		-	-	-	-

Table 1 (part II)

		Present invention						
Example No.		14	15	16	17	18	19	20
Composition (wt%)	Fe	77.5	76	76	63	72	85	70
	Al	2.5	4	12	12	3	3	8
	Cr	20	20	12	25	25	12	22
Batch composition (wt%) (300 mesh or less)	Fe Powder	55	52	52	26	49	70	60
	Al Powder							
	Cr Powder					5		
	Fe-50Al Powder	5	8	24	24	6	6	16
	Fe-50Cr Powder	40	40	24	50	40	24	44
Sintering temperature (°C) (Hydrogen atmosphere.)		1250	1400	1400	1450	1370	1350	1430
Heat-treatment temperature (°C)		1100	1100	1050	1100	1100	1050	1100
Porosity (%)		25	8	22	10	12	13	9
Resistance to oxidation (wt%) (An increase in weight caused by thermo-aging 1000 hours at 900° C)		9.7	1.0	3.0	1.9	4.8	7.1	2.0
Resistance to corrosion(X) (Reduction of weight caused by dipping 1 hour in HCl solution of pH1)		-	-	-	-	-	-	-

Example 2

Fe powder, Al powder, Cr powder, Fe-Al alloy powder and Fe-Cr alloy powder, having a particle size of 300 mesh or less and prepared in the same manner as Example 1, were mixed with Cu powder and Sn powder, having a particle size of 300 mesh or less, to prepare various powder mixtures having the compositions listed in Table 2, and honeycomb structures were manufactured using those mixtures in the same manner as that of Example 1.

The porosity and oxidation resistance of the obtained honeycomb structures were measured. The results of the measurements are shown in Table 2.

As is clear from Table 2, addition of Cu and Sn powders lowers the sintering temperature or decreases the porosity in the case of the sintering performed at the same temperature. However, introduction of Cu and Sn powders deteriorates oxidation resistance, and should therefore be restricted less than 10% by weight in total.

Table 2

Example No.	Present Invention		Reference	Present Invention		Reference	Present Invention		Reference		Present Invention		
	21	22		23	24		25	26	27	28	29	30	31
Composition (wt%)	Fe	70	65	60	70	85	5	65	63	65	70	71	70
	Al	5	5	5	5	5	5	5	5	5	5	24	5
	Cr	20	20	20	20	20	20	20	20	20	20		20
	Cu	5	10	15				5	6	5	4.5	4.5	4.5
	Sn				5	10	15	5	6	5	0.5	0.5	0.5
Batch composition (wt%)	Fe powder	45	40	35	45	40	35	40	38	40	45	47	45
	Fe-50Al powder	10	10	10	10	10	10	10	10	10	10	48	10
	Fe-50Cr powder	40	40	40	40	40	40	40	40	40	40		40
	(300mesh or less)	5	10	15				5	6	5	4.5	4.5	4.5
	Cu powder				5	10	15	5	6	5	0.5	0.5	0.5
Sn powder													
Sintering temperature (°C) (hydrogen-argon atmosphere)	1100	1100	1050	1100	1100	1100	1050	1050	1050	950	1300	1300	1350
Heat-treatment temperature (°C)	1000	1000	950	1000	1000	1000	950	1000	1000	900	1050	1000	1100
Porosity (%)	32	28	30	35	30	30	31	26	24	36	8	7	5
Resistance to oxidation (wt%) (An increase in weight caused by thermo-aging 1000 hours at 900°C)	5.3	7.1	12.3	5.9	7.7	11.9	11.9	6.9	10.6	13.4	2.8	2.9	2.3

Example 3

Sintered materials each consisting of a honeycomb structure having either of the following compositions were prepared using an extrusion die having 4 mil in rib thickness and 400 per cm^2 in number of through-holes, according to the same method as in Example 1.

(1) Fe-20Cr-5Al

(2) Fe-23Al

Then, there were investigated preferable conditions for treating each of the above sintered materials to form a film thereon.

Incidentally, the sintered materials having a Fe-20Cr-5Al composition were obtained by firing an iron carbonyl powder, a ground Fe-50Al powder and a ground Fe-60Cr powder at $1,320^\circ\text{C}$; the sintered materials of a Fe-23Al composition were obtained by firing an iron carbonyl powder and a ground Fe-50Al powder at $1,320^\circ\text{C}$.

The furnace used for treating each sintered material of honeycomb structure (Run Nos. 38-43) was a 300-liter gas furnace of internal heating type comprising a W mesh heater and a Mo reflector. The gas flow rate employed was 1-10 liters/min. In Run Nos. 38-43, there was used a hydrogen gas or a hydrogen-nitrogen mixture gas, in each of which gases the water content had been controlled.

The sintered materials of honeycomb structure having a film thereon were subjected to an oxidation resistance test by keeping them in an electric furnace at $1,000^\circ\text{C}$ for 100 hours to evaluate their weight increases and dimensional changes. The results are shown in Table 3. The surface films after the oxidation resistance test were observed by a SEM (scanning type electron microscope). Each film caused no peeling and had good adhesion.

Total oxidation amount was approximately expressed as a sum of [weight increase by preliminary oxidation (oxide film formation)] and [weight increase by oxidation resistance test ($1,000^\circ\text{C} \times 100$ hours)].

As is clear from Table 3, comparison of Run Nos. 33-34 (Comparative Examples) with Run Nos. 35-38-40 (Examples) indicates that the total oxidation amounts of the Examples are smaller than those of the Comparative Examples and that protective film of superior oxidation resistance were formed in the Examples. Comparison of Run Nos. 36-37 (Comparative Examples) with Run Nos. 41-43 (Examples) indicates the same thing.

Table 3

	Comparative Example		Present Invention	Comparative Example		Present Invention						
	33	34		35	36	37	38	39	40	41	42	43
Run No.	75	75	75	75	77	77	75	75	75	77	77	77
Composition (wt%)	5	5	5	5	23	23	5	5	5	23	23	23
	20	20	20	20	0	0	20	20	20	0	0	0
Porosity (%)	30	30	30	30	35	35	30	30	30	35	35	35
Temperature of keeping (°C)	No heat treatment	500	1000	1000	No heat treatment	500	1000	1300	1000	1000	1300	1000
Conditions of treatment		5	5	5		5	5	5	5	5	5	5
Time of keeping (hr)												
Introduced gas	No heat treatment	In air	In air	In air	No heat treatment	In air	Hydrogen	Hydrogen	Hydrogen 3 : Nitrogen 1	Hydrogen	Hydrogen	Hydrogen 3 : Nitrogen 1
Dew point (°C)							-40	-60	-70	-40	-60	-70
Weight increase by preliminary oxidation (wt%)	-	0.1	1.3		-	0.1	0.5	(0.1	0.8	0.6	0.2	1.4
Oxidation resistance	3.4	3.3	1.9		6.3	6.2	2.0	2.3	1.6	2.3	3.0	1.4
Dimensional change (diaz) (1000 °C×100hr)	1.0	1.4	1.0		3.8	3.8	1.0	1.1	1.0	1.4	0.8	0.6
Total oxidation amount (wt%)	3.4	3.4	3.2		6.3	6.3	2.5	2.3	2.6	2.9	3.2	2.8

Example 4

There were mixed an iron carbonyl powder of 5 μm in average particle diameter, a ground Fe-Al alloy powder of 26 μm in average particle diameter, an electrolytic Cr powder of 43 μm in average particle diameter, an
5 atomized Fe-30 Cr alloy powder of 20 μm in average particle diameter and a ground Fe-60CR alloy powder of 18 μm in average particle diameter so as to give a composition shown in Table 4. Each mixture was subjected to the same procedure as in Example 1 to prepare a honeycomb structure.

Each of the honeycomb structures was measured for porosity and oxidation resistance in the same manner as in Example 1. The results are shown in Table 4.

10 As is clear from Table 4, use of 30% by weight or more of an iron powder in material powder gives improved oxidation resistance and corrosion resistance.

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Table 4

Example No.	Present invention							
	44	45	46	47	48	49	50	51
Composition (wt%)								
Fe	75	73	66	75	71	75	74	79
Al	5	5	8	5	3	5	8	5
Cr	20	22	26	20	26	20	18	18
Batch Composition (wt%)								
Fe Powder	70	68	40.7	56.7	50.7	23.3	24	30
Fe-50Al Powder	10	10	16	10	6	10	16	10
Cr Powder	20	22			5			
(300 mesh or less)								
Fe-30Cr Powder						66.7	60	60
Fe-60Cr Powder			43.3	33.3	43.3			
Sintering temperature (°C) (Hydrogen atmosphere)	1300	1350	1350	1350	1400	1300	1300	1400
Heat-treatment temperature (°C)	1050	1100	1050	1100	1000	1000	1000	960
Porosity (%)	21	16	29	30	16	21	37	19
Resistance to oxidation (wt%) (An increase in weight caused by thermo-aging 1000 hours at 900°C)	2.1	1.6	2.8	2.5	3	4.1	4.6	3.5
Resistance to corrosion (%) (Reduction of weight caused by dipping 1 hour in HCl solution of pH1)	0.2	0.1	0.3	0.2	0.2	1.2	1.7	0.7

Example 5

Fe powder, Fe-Al powder (Al : 50 wt%) and Fe-Cr powder (Cr : 50 wt%), having average particle sized of 10, 20 and 22 μm , were mixed to prepare a mixture having a composition of Fe-22Cr-5Al (% by weight), and the obtained mixture was then blended into an organic binder (methyl cellulose), an antioxidant (ol ic acid) and water to produce a readily formable body. That body was formed into a square cell honeycomb structure having a rib thickness of 4 mil and a cell density of 300 cm^2 by extrusion. The extruded honeycomb structure was dried and fired in H_2 atmosphere at 1300°C. Thereafter, the obtained honeycomb structure was subjected to heat-treatment in atmosphere at 1000°C. One electrode was provided on the central axis of the obtained honeycomb

structure while the other electrode was provided on the outer periphery thereof.

The obtained honeycomb structure had a porosity of 22% by volume and an average pore diameter of 5 μm .

5 Example 6

A honeycomb structure with a catalyst supported thereon was obtained by coating $\gamma\text{-Al}_2\text{O}_3$ on the honeycomb structure obtained in Example 5, by loading 20 g/ft² Pt and Pd respectively and then by firing the whole at 600°C. thereafter, the electrodes were provided in the same manner as that of example 5.

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Example 7

A honeycomb structure having a composition of Fe-25Al was obtained in the same manner as that of Example 5. This honeycomb structure had a porosity of 25% by volume and an average pore diameter of 4 μm .

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Example 8

A honeycomb structure with a catalyst carried thereon was obtained in the same manner as that of Example 6 using the honeycomb structure obtained in Example 7.

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Comparative Example 1

Electrodes were provided on a foil-type metal honeycomb (having a rib thickness of 2 mil, a passage density of 400 cpi², and a composition of Fe-20Cr-5Al) which was on sale.

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Comparative Example 2

The sample of Comparative Example 1 was subjected to oxidation in the manner described in U.K. Patent 1492929. The oxidation was conducted by maintaining the sample in the air at a temperature of 1000°C for 1 hour, and a catalyst was supported on that sample in the same manner as that of Example 6.

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[Evaluation]

35 (Heat cycle durability test)

With the use as a preheater for a catalyst for use in automobile exhaust emission control in mind, supply of a current by battery of 12V for 30 seconds was repeated 300 times while an air was caused to flow through the passages at a rate of 1.0m³/min. The temperature of the cell walls reached about 400 to 500°C.

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(Catalyst peeling test)

Table 5 shows a change in the weight of the catalyst, caused by the heat cycle durability test, and Table 6 shows a change in the weight of the sample subjected to the heat cycle test, caused for forcibly causing the catalyst to peel by the ultrasonic washing.

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Table 5 Rate of change in the catalyst weight
caused by the heat cycle durability test

Sample	Rate of reduction in weight(%)
Example 6	0.8
Example 8	0.6
Comparative Example 2	3.5

Table 6 Amount of catalyst which peels of the
sample subjected to the heat cycle durability test

Sample	Rate of reduction in weight (%)
Example 6	1.2
Example 8	0.8
Comparative Example 2	10.2

when the foil type metal honeycomb was subjected to heat cycle durability test, the flat plate to corrugated plate join was cracked and telescope phenomenon occurred whereas no change was seen on the samples of Examples of the present invention.

(Heat generation checking test)

A current was supplied to the samples subjected to the heat cycle durability test using a battery of 12V for 30 minutes while an air was caused to flow at a rate of 1.0 m³/min. At that time, the temperature of the cell walls located near the center of the honeycomb structure was measured at 5 points. Table 7 shows the time required for the temperature to reach 350°C.

Table 7

Sample	Time required (sec)
Example 5	8.5
Example 6	10.0
Example 7	9.5
Example 8	11.5
Comparative Example 1	14.0
Comparative Example 2	16.5

In Examples 5 to 8, temperature distribution was within the range of $\pm 20^{\circ}\text{C}$ while in Comparative Examples it was within the range of $\pm 50^{\circ}\text{C}$.

(Checking for the performance required for a preheater for use in automobile exhaust emission control)

The catalytic converters were obtained by providing as a preheater each of the samples of this invention in from of a three-way catalyst which was on sale. An exhaust gas of the engine was introduced to each con-
 5 verter for 2 minutes to raise the temperature thereof from 100°C up to 420°C at a fixed speed and the tempera-
 ture was then kept at 420°C for 1 minutes. The conversion of the components present in the exhaust at that
 time was measured to check the performance of the above-described catalytic converters when an engine was
 started.

The samples subjected to the heat cycle test were used as the heaters in a state in which they were ener-
 10 gized for 1 minutes by a battery of 12V. Table 8 shows the average conversion of the component gases
 measured for three minutes.

Table 8 Average Conversion (%)

Sample	CO	HC	NO _x
Without heater	50	37	47
Example 5	62	47	60
Example 6	68	52	65
Example 7	62	46	59
Example 8	67	50	64
Comparative Example 1	56	42	53
Comparative Example 2	60	45	55

Claims

1. A heat-resistant metallic monolith comprising:
 a metal monolith manufactured by forming metal powders into a shape of a honeycomb configuration
 35 and by sintering said shape; and
 a heat-resistant metal oxide coated on a surface of cell walls and that of pores in said metal monolith.
2. A heat-resistant metallic monolith according to claim 1, wherein said metal monolith consists essentially
 of 2.5 to 30% by weight of Al, 0 to 40% by weight of Cr and a balance of Fe.
3. A heat-resistant metallic monolith according to claim 1, wherein said metal monolith consists essentially
 40 of 2.5 to 30% by weight of Al, 0 to 40% by weight of Cr, 0 to 10% by weight of Sn, 0 to 10% by weight of
 Cu, the sum Sn and Cu being up to 10% by weight, and a balance of Fe.
4. A catalyst carrier comprising a heat-resistant metallic monolith according to claim 1.
5. A honeycomb heater comprising;
 a metallic honeycomb structure produced by forming metal powders into a honeycomb configuration
 and by sintering said honeycomb; and
 50 at least two electrodes through which a current is supplied to said honeycomb structure to heat gas
 flow in passages formed in said honeycomb structure.
6. A honeycomb heater comprising:
 a heat-resistant metallic monolith comprised of a metal monolith manufactured by forming metal
 55 powders into a shape of a honeycomb configuration and by sintering said shape, and a heat-resistant metal
 oxide coated on a surface of cell walls and that of pores in said metal monolith; and
 electrodes provided on said metallic monolith.

7. A catalytic converter comprising:
 - a main monolith catalyst; and
 - a honeycomb heater disposed adjacent to and upstream of said main monolith catalyst, said honeycomb heater including a metallic honeycomb structure produced by forming metal powders into a honeycomb configuration and by sintering said honeycomb, and at least two electrodes provided on said metallic honeycomb structure.
8. A catalytic converter comprising:
 - a main monolith catalyst;
 - a heater disposed adjacent to and upstream of said main monolith catalyst, said heater including a heat-resistant metallic monolith comprised of a metal monolith manufactured by forming metal powders into a shape of honeycomb configuration and by sintering said shape and a heat-resistant metal oxide coated on a surface of cell walls and that of pores in said metal monolith; and electrodes provided on said heat-resistant metallic monolith.
9. A catalytic converter comprising:
 - a main monolith catalyst; and
 - a heater disposed adjacent to and upstream of said main monolith catalyst, said heater including a heat-resistant metallic monolith comprised of a metal monolith manufactured by forming metal powders into a shape of a honeycomb configuration and by sintering said shape, and a heat-resistant metal oxide coated on a surface of cell walls and that of pores in said metal monolith;
 - a catalyst supported on said heat-resistant metallic monolith; and
 - electrodes provided on said heat-resistant metallic monolith.
10. A catalytic converter comprising:
 - a heat-resistant metallic monolith comprised of a metal monolith manufactured by forming metal powders into a shape of a honeycomb configuration and by sintering said shape and a heat-resistant metal oxide coated on a surface of cell walls and that of pores in said metal monolith;
 - a catalyst supported on said heat-resistant metallic monolith; and
 - electrodes provided on said heat-resistant metallic monolith.
11. A method of manufacturing a heat-resistant metallic monolith, comprising the steps of:
 - mixing metal powders, an organic binder and water to prepare a mixture;
 - forming said mixture into a shape of a desired honeycomb configuration;
 - sintering said shape in a non-oxidizing atmosphere at a temperature between 1000 and 1450°C;
 - and
 - coating a heat-resistant metal oxide on a surface of cell walls and that of pores of the obtained sintered body.
12. A method of manufacturing a heat-resistant metallic monolith according to claim 11 wherein said metal powders are a mixture consisting essentially of 2.5 to 30% by weight of Al, 0 to 40% by weight of Cr and a balance of Fe.
13. A method of manufacturing a heat-resistant metallic monolith according to claim 11, wherein said metal powders are a mixture consisting essentially of 2.5 to 30% by weight of Al, 0 to 40% by weight of Cr, 0 to 10% by weight of Sn, 0 to 10% by weight of Cu, the sum Sn and Cu being up to 10% by weight, and a balance of Fe.
14. A method of manufacturing a heat-resistant metallic monolith according to claim 11, wherein the metal powder material comprises at least 30% by weight of a pure iron powder.
15. A method of manufacturing a heat-resistant metallic monolith according to claim 14, wherein the pure iron powder is an iron carbonyl powder.
16. A method of manufacturing a heat-resistant metallic monolith according to claim 11, which comprises keeping the sintered body in a hydrogen-containing gas atmosphere of 500-1,300°C to form a heat-resistant metal oxide thereon.

17. A method of manufacturing a heat-resistant metallic monolith according to claim 16, wherein the hydrogen-containing gas atmosphere has a dew point of -70°C to -40°C .

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FIG.1

